Effects of Associated Anion on Hydrophilicity of Quaternary Ammonium Cellulose

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Synopsis

Quaternary ammonium celluloses, formed by introduction of cations and anions in nonaqueous media, were used to elucidate effects of associated ions on the hydrogen-bonded cellulose–water matrix. Exchangers were characterized by wet analyses, potentiometric and conductometric titrations, and by ESCA. Techniques of optical and electron microscopy were used to observe exchangers when immersed in water. A given quaternary ammonium cellulose is more soluble or dispersible in water when its anion is large and hydrophobic as is iodide or thiocyanate. When associated with the small chloride ions that are hydrated, the quaternary exchangers do not disperse regardless of cation size. All exchangers with crosslinked quaternary groups are insoluble. Data indicate that accommodation of a large hydrophobic cation and hydrophobic, polarizable anion within a cagelike structure surrounded by water more highly structured than bulk water results in swelling and dispersion.

INTRODUCTION

Anion exchange cottons that contain quaternary ammonium cationic groups have been prepared by a variety of methods. These strong base anion exchangers in the fabric form have been analyzed by instrumental techniques that included potentiometric and conductometric titrations.[1,2] More recently, there is renewed interest in effects of quaternary ammonium (Q) substituents in cellulose. In the industry, Q groups are being introduced by reacting cotton with glycidyl trimethyl ammonium chloride, a compound originally manufactured by Shell Chemical Company[3] and studied by McKelvey and coworkers.[4,5] Even before the compound was isolated, Stahn[6] patented a process that allowed for wool dyes to be fixed on cottons by reacting cotton with ammonia, epichlorohydrin, and 2% NaOH under reduced pressures. Products of the reaction between cotton and glycidyl trimethyl ammonium chloride, even at low degrees of substitution, improve the dyeability of cottons and their penetration by finishing reagents in aqueous media. These Q groups not only attract anions and water-soluble reagents, but have been found to scavenge both hydrophilic and hydrophobic moieties. A cellulosic product called "grab rag" designed for use in launderings has been patented.[7] The "grab rag," a quaternized cellulose, scavenges dye particles released from colored fabrics and allows whites to be laundered with colored fabrics.

Early research by Meredith[8] indicated the importance of moisture regain and the manner in which water is held on the physical properties of cotton. He noted that, in general, cotton fibers increase in length by about 1.2% and increase in diameter by about 14% when going from the dry to the wet state in water. Initially, the first water absorbed is tightly held and differs from that

CCC 0021-8995/88/061255-27$04.00

taken up at higher regains. The density of cotton increases with respect to the dry cottons and then decreases as the moisture regain increases. It was also early appreciated that the presence of salts in aqueous solutions affects the amounts and types of water taken up by cottons. The lyotropic series has long been used to explain effects of salts on swelling of cotton by water. In earlier work, cations have been in the solvent and not a part of the cellulose matrix as in this study. This is a report of a study of the interaction of water with cotton fibers containing a variety of Q groups as revealed by optical and electron microscopy. In particular, the effect of the anion associated with the Q group is revealed.
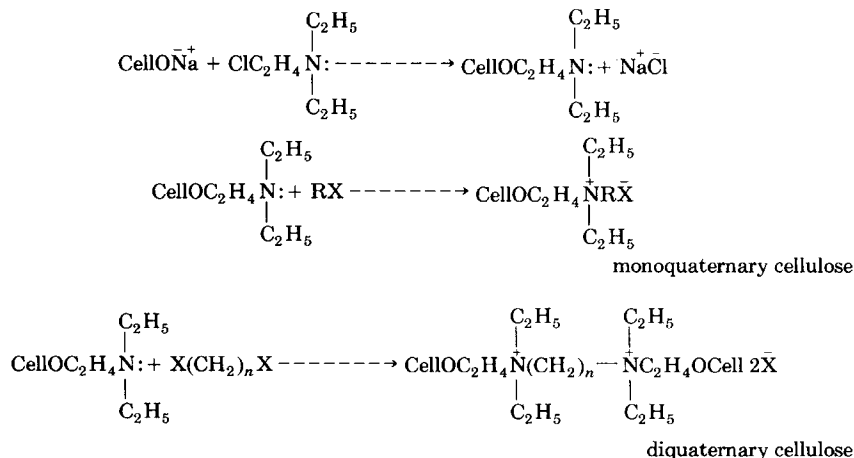
EXPERIMENTAL

Reagents

Alkyl halides, dihaloalkanes, and tertiary butanol were reagent-grade chemicals from Eastman Organic Chemicals; β-chloroethylamine hydrochloride and dimethylformamide were reagent grade chemicals from Matheson, Coleman, and Bell, absolute methanol was from Mallinckrodt Chemical Works.*

Fabrics

Preparations of diethylaminoethyl–celluloses (DEAE–cellulose) in fabric form have been reported.[9,10] To prepare a DEAE–cellulose of approximately 0.6% N, cotton was reacted with 0.2M sodium methoxide and the resultant sodium cellulosate was reacted for 5 h with a 3% weight solution of β-chloroethyldiethylamine in t-butanol. A DEAE fabric of 3.0% N required a 1.25M sodium methoxide solution and reaction for 24 h in the β-chloroethyldiethylamine solution.

DEAE–cottons in the free amine form were washed free of t-butanol with absolute methanol and then refluxed for 5 h in ethanolic solutions of about 10–20% of the alkyl halide or dihaloalkane to prepare the monoquaternary or diquaternary ammonium cellulose exchangers, respectively.

The following equations describe the preparations:

$$CellON\overset{-}{a}{}^{+} + ClC_2H_4\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{N}}: ------- \rightarrow CellOC_2H_4\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{N}}: + Na\overset{+}{}\overset{-}{Cl}$$

$$CellOC_2H_4\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{N}}: + RX ------- \rightarrow CellOC_2H_4\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{\overset{+}{N}}}R\overset{-}{X}$$

monoquaternary cellulose

$$CellOC_2H_4\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{N}}: + X(CH_2)_nX ------- \rightarrow CellOC_2H_4\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{\overset{+}{N}}}(CH_2)_n --- \underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{\overset{+}{N}}}C_2H_4OCell\ 2\overset{-}{X}$$

diquaternary cellulose

Exchange of Anions

Exchange of the original ion furnished by the alkyl halide or dihaloalkane was accomplished in nonaqueous media. Exchange of anions was in absolute alcohol or dried dimethylformamide. For example, in nonaqueous media, a QI was exchanged to QCl, then to QSCN or QBH_4 as desired.

Analysis

Nitrogen contents were by the Kjeldahl method and reported on meq/g fabric and/or wt %. Relative percentages of tertiary amine groups (as in DEAE–cottons) and of quaternized groups were determined by techniques of electron emission spectroscopy for chemical analysis (ESCA)[11] by potentiometric titration and/or conductometric titration.[1,2] Conventional wet analyses were used to analyze for various anions.

Microscopical Examinations

Fiber examinations by techniques of optical microscopy have been described.[12] Scanning electron micrographs of fibers of selected samples before and after subjection to solvents were made.[13] Cross sections of a few fibers were subjected to energy dispersive X-ray (EDX) analysis to determine distribution of a given element in the chemically modified cottons.

RESULTS AND DISCUSSION

Monoquaternary ammonium cellulose salts varying in N contents from 0.8% to 4.0% were exchanged in nonaqueous media so that fabrics in the chloride, bromide, iodide, thiocyanate, and borohydride anion forms were prepared. Data in Table I are typical of monoquaternary salts. In the absence of water, all fabrics were intact and revealed no obvious differences. In the presence of water, particularly for those of high N content, the thiocyanates and borohydrides were most soluble. In fact, the thiocyanates of high N content absorb

TABLE I
Monoquaternary Ammonium Cellulose Exchangers

| Cellulose products | Solubilities | | | | Conversion (%) | Composition (%) | |
	H_2O	CH_3OH	Glycerol	Cuene		N	X^a
1. Mercerized cotton	−	−	−	+			
2. DEAE–cotton	−	−	−	+		2.40	
3. DEAE–cotton	−	−	−	+		0.8	
4. QI from 2[b]	−			+	100	2.47	20.55
5. QCl from 4[b]	−			+	96	2.45	6.00
6. QBr from 4[b]	−			+	98	2.41	13.50
7. QBH_4 from 4[b]	+ +	−	sl	+	100	2.69	2.00
8. QSCN from 4[b]	+ +	−	sl	+	100	2.70	3.14
9. QI from 3[b]	−	−	−	+	75	0.8	6.5

[a] X represents halogen, B or S.
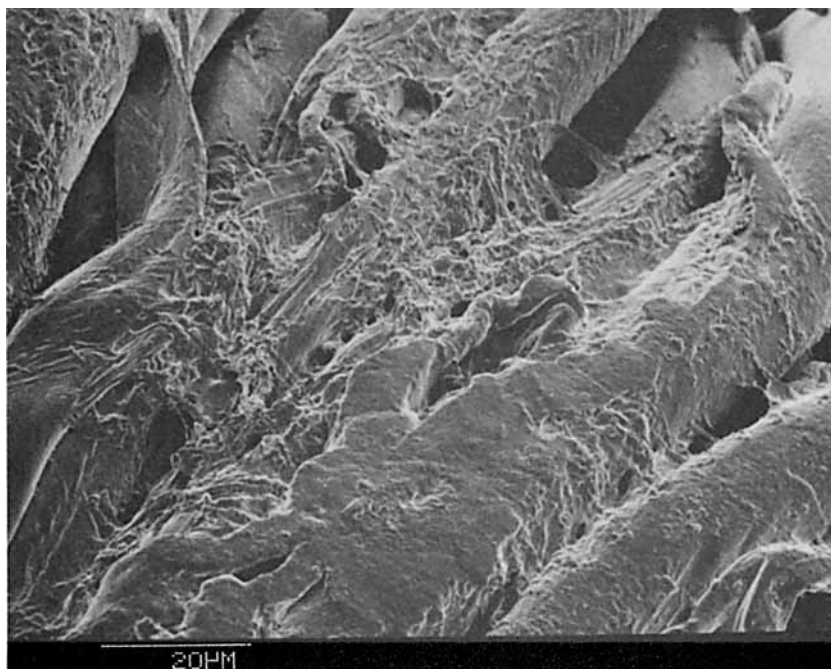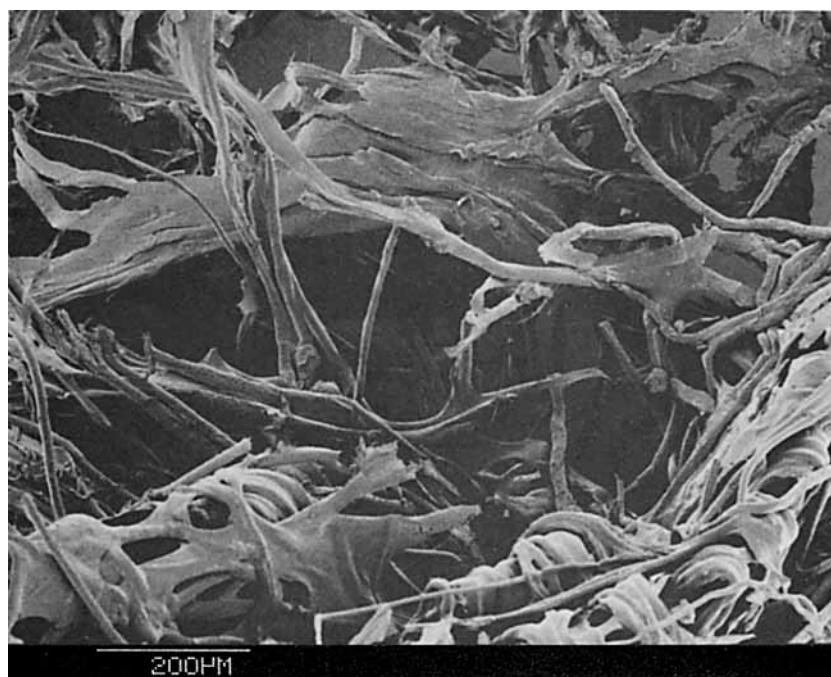[b] Q is quaternary ammonium constituent.
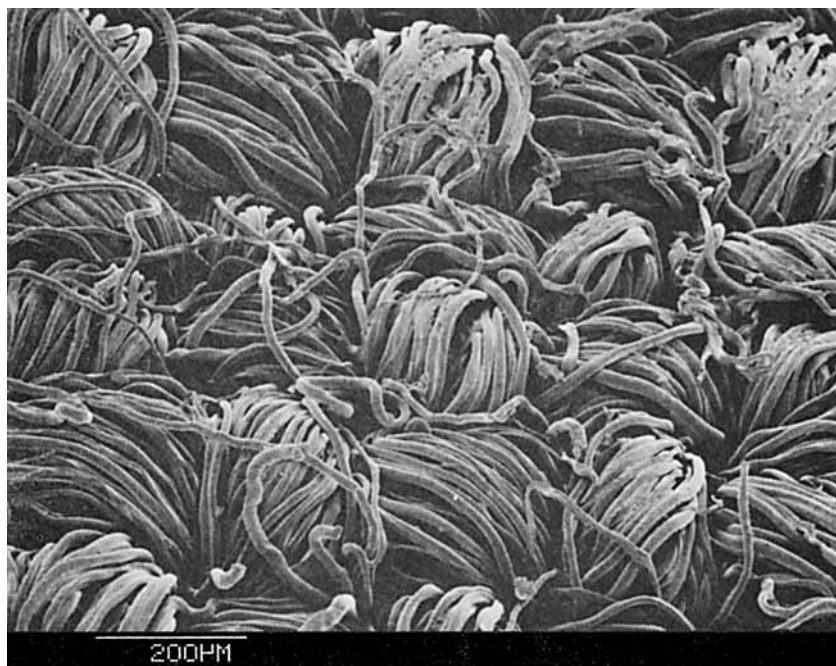
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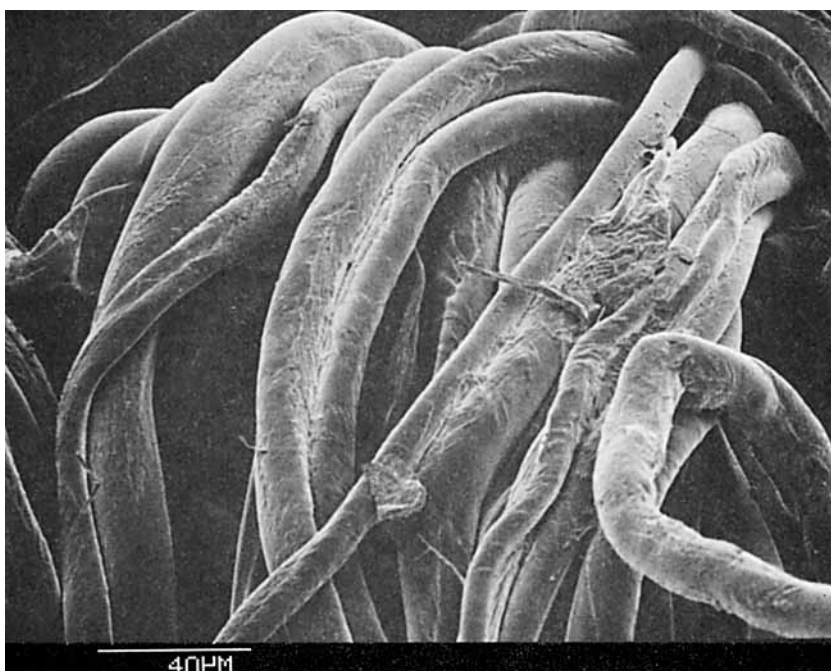
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Fig. 1. Scanning electron micrographs of methyldiethylaminoethylammonium cellulose chloride prepared nonaqueously and then immersed in water.
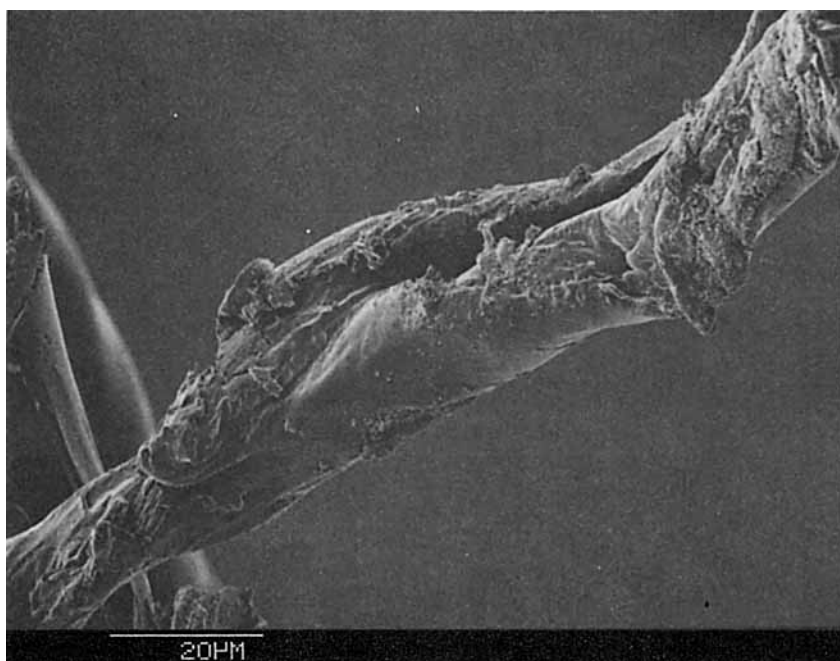
(c)

Fig. 1. (*Continued from the previous page.*)

(a)

Fig. 2. Scanning electron micrographs of methyldiethylaminoethylammonium cellulose thiocyanate prepared nonaqueously and then immersed in water.
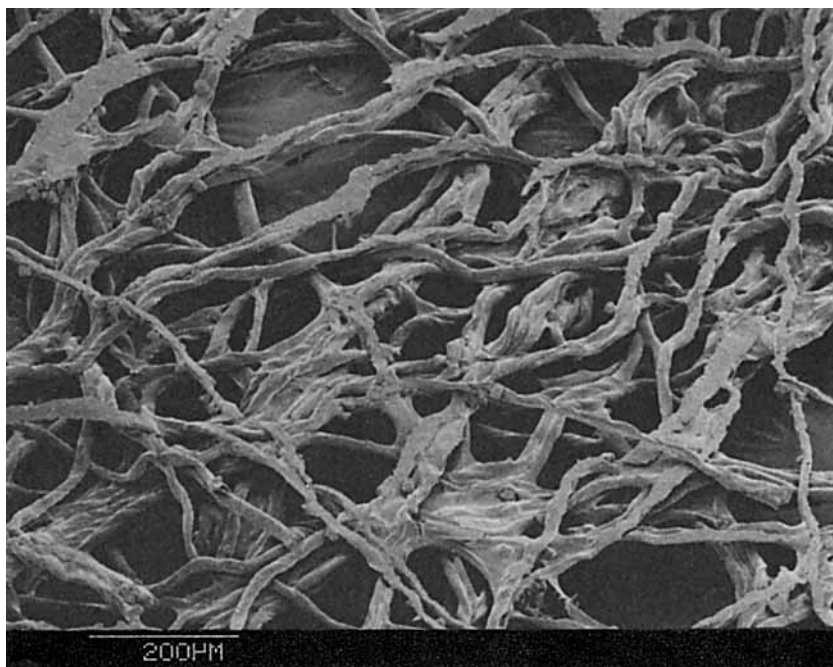
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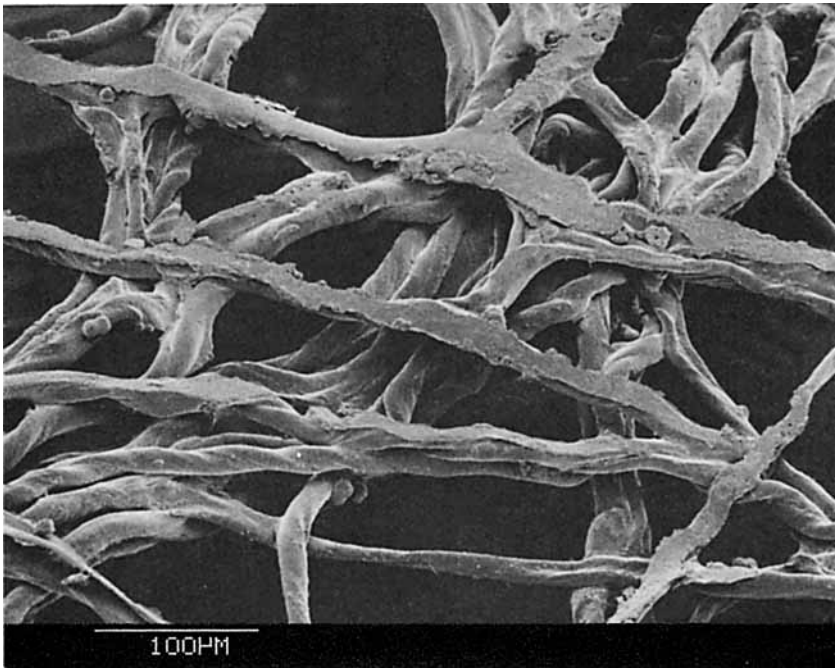Fig. 2.　(*Continued from the previous page.*)

(a)

Fig. 3.   Scanning electron micrographs of methyldiethylaminoethylammonium cellulose boro-
hydride prepared nonaqueously and then immersed in water.

water so rapidly that when a small piece of fabric is placed in a beaker of
water, swelling action is so vigorous that yarns are separated from the fabric
and untwisted, leaving only small fiber fragments suspended in the water.

Scanning electron micrographs (Figs. 1, 2, and 3) illustrate effects of water
on fabric structures. These samples represent a DEAE cotton of 2.64% N that
had been quaternized with CH_3I and exchanged to the chloride (Fig. 1),
thiocyanate (Fig. 2), and borohydride (Fig. 3) forms in nonaqueous media.
After contact with water, fabrics in the thiocyanate and borohydride forms
were partially dissolved and reprecipitated immediately. Fibers in the chloride
form were washable in water and retained the fabric structure.

Optical micrographs in Figures 4 and 5 depict fibers in mineral oil and in
water. Included are controls of the mercerized fabric and the DEAE–cotton
fabric used to prepare the quaternaries and a monoquaternary chloride (Fig.
4). Fibers in bromide, iodide, thiocyanate, and borohydride forms of the
quaternary cellulose exchangers are included in Figure 5. All of these fibers
were soluble in 0.5M cuene.

Reactions of DEAE–cottons with dihaloalkanes form diquaternary am-
monium salts that do not dissolve in water and or in cuene. In Table II are
selected diquaternary ammonium celluloses and their degree of conversion as
determined by three methods. Even at a low degree of substitution (0.67% N)
reaction with diiodopentane forms a diquaternary exchanger whose fibers are
insoluble in water and only slightly soluble in 0.5M cuene (Fig. 6) Di-

(b)
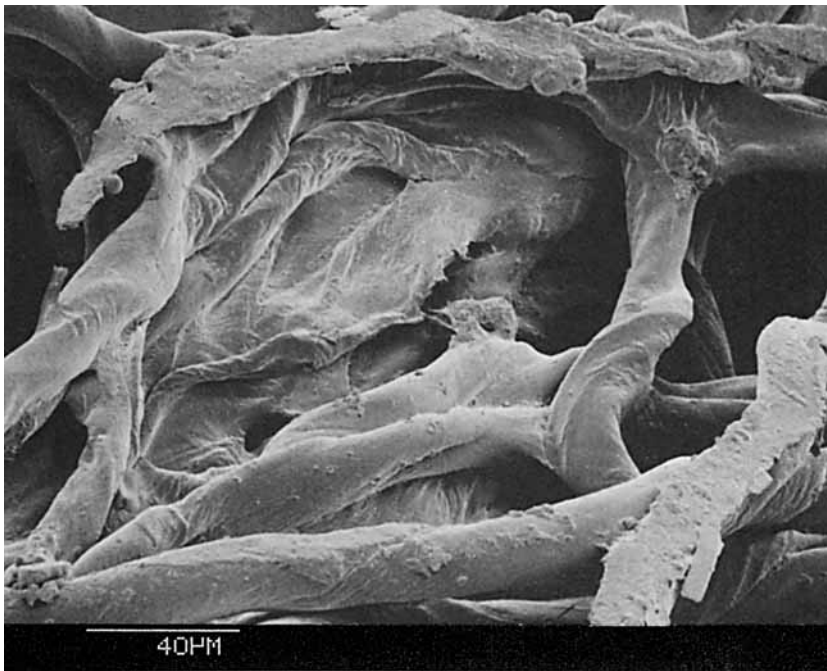
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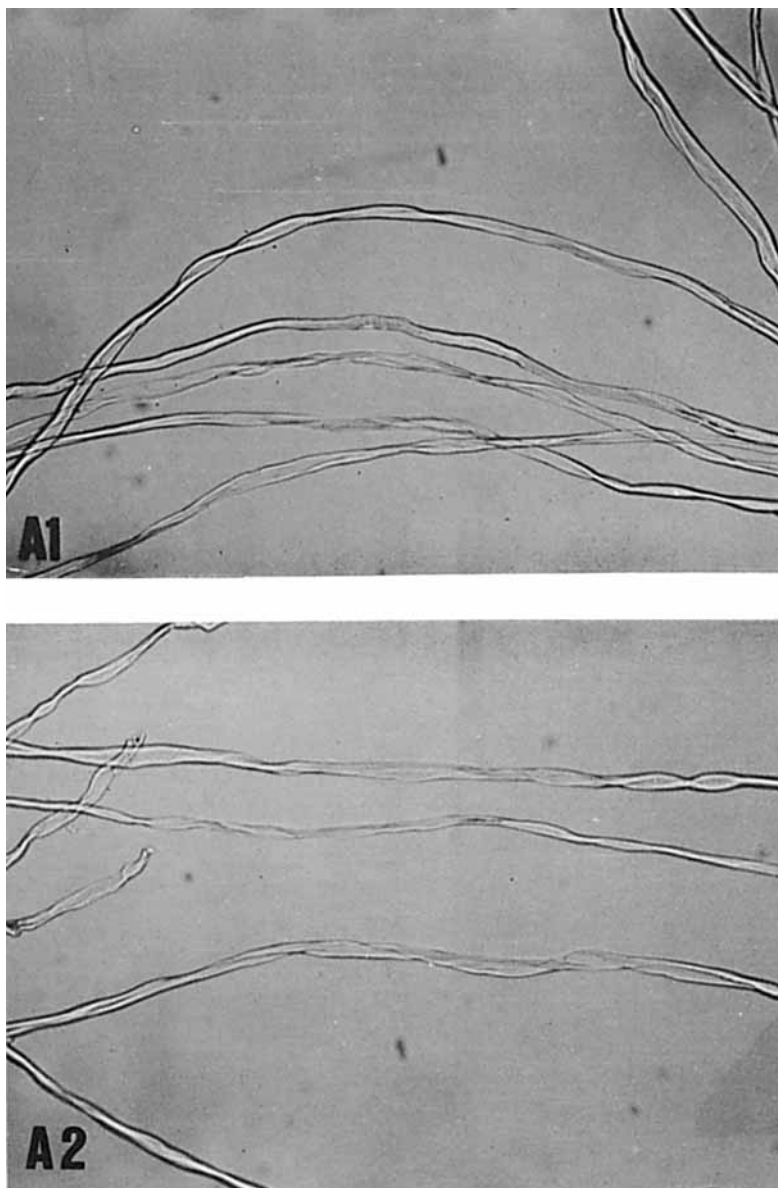Fig. 3.   (*Continued from the previous page.*)

Fig. 4. Optical micrographs of fibers in mineral oil (A) and in water (B) from a mercerized cotton (1), a DEAE–cotton (2), and a monoquaternaryammonium cellulose in the chloride form (QCl) (3).
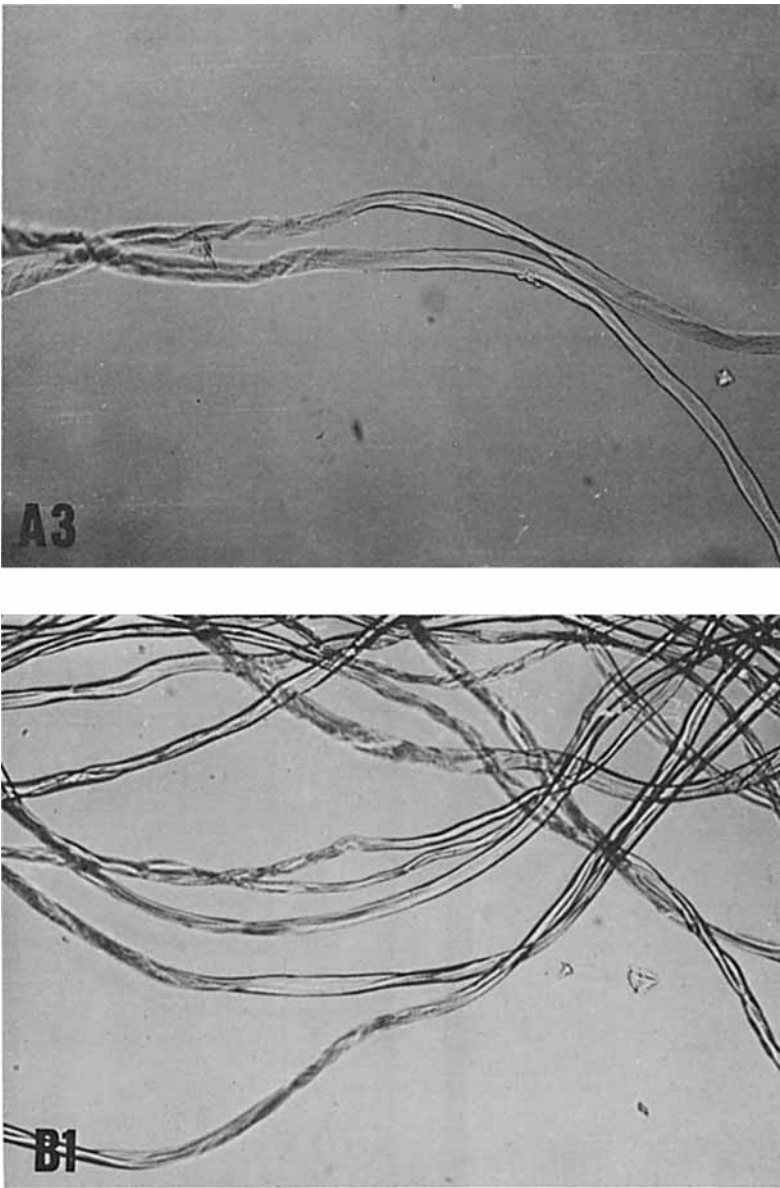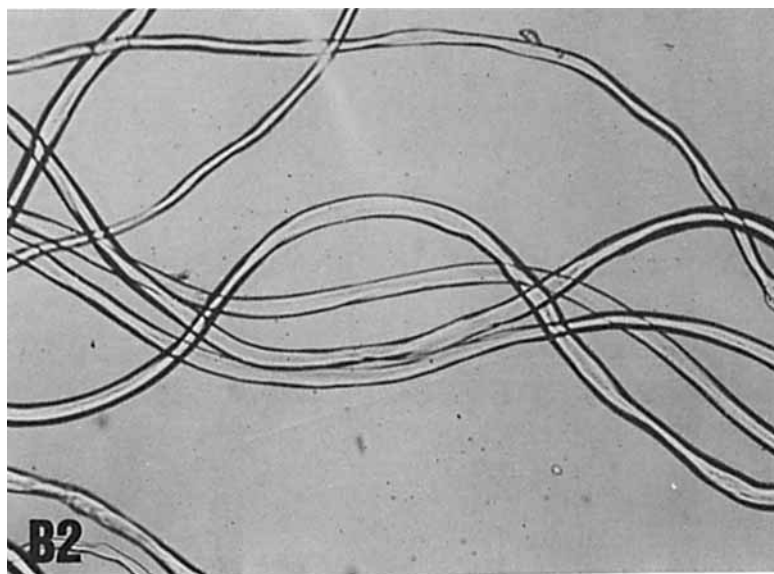
Fig. 4. (*Continued from the previous page.*)
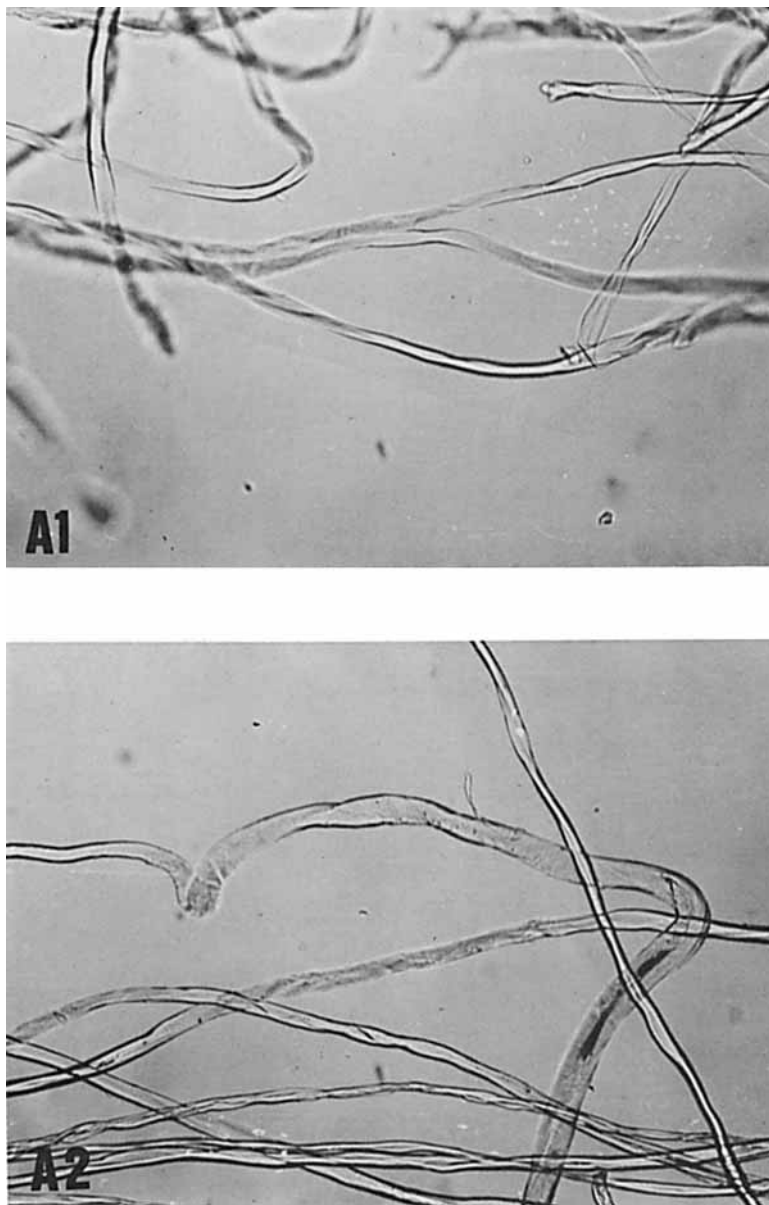
Fig. 4.   (*Continued from the previous page.*)

Fig. 5.   Optical micrographs of fibers in mineral oil (A) and in water (B) from the mono-quaternaryammonium celluloses in the bromide (1), iodide (2), thiocyanate (3), and borohydride (4) forms.
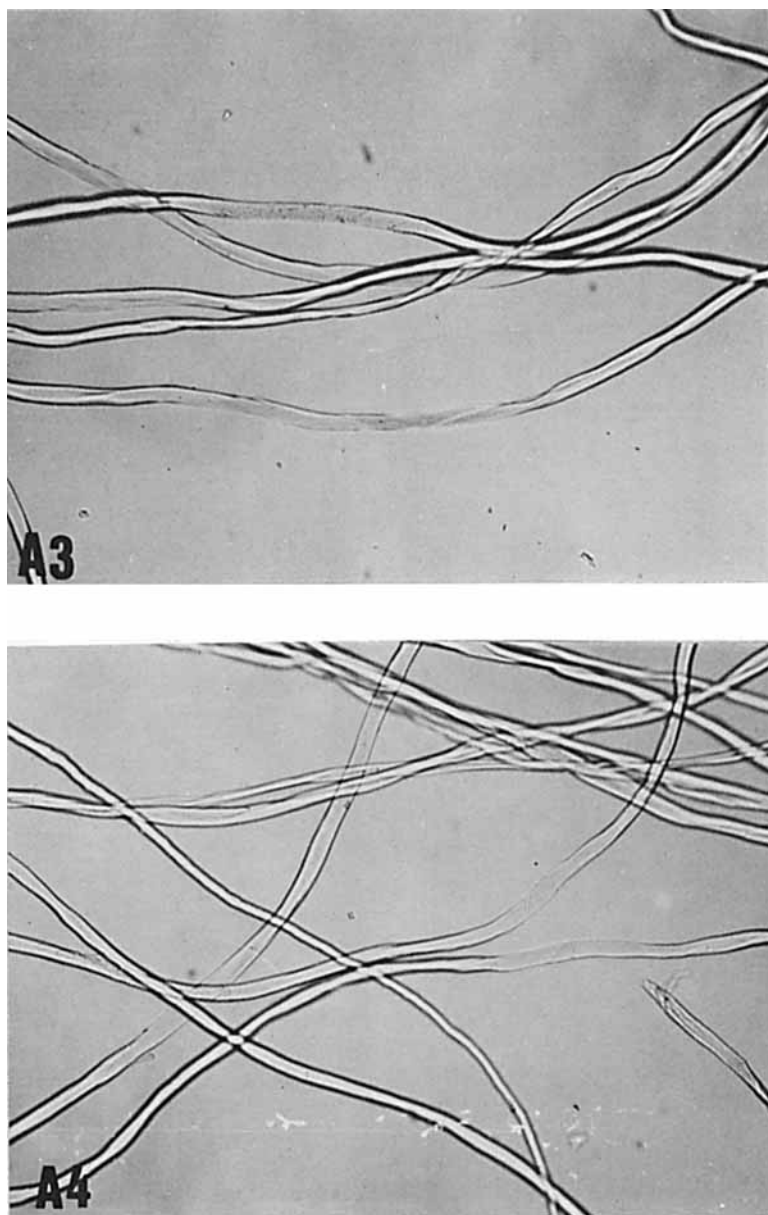
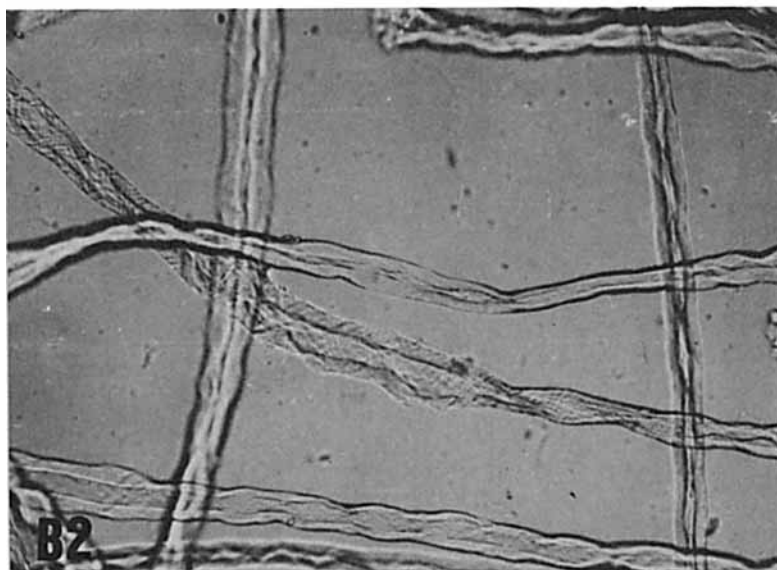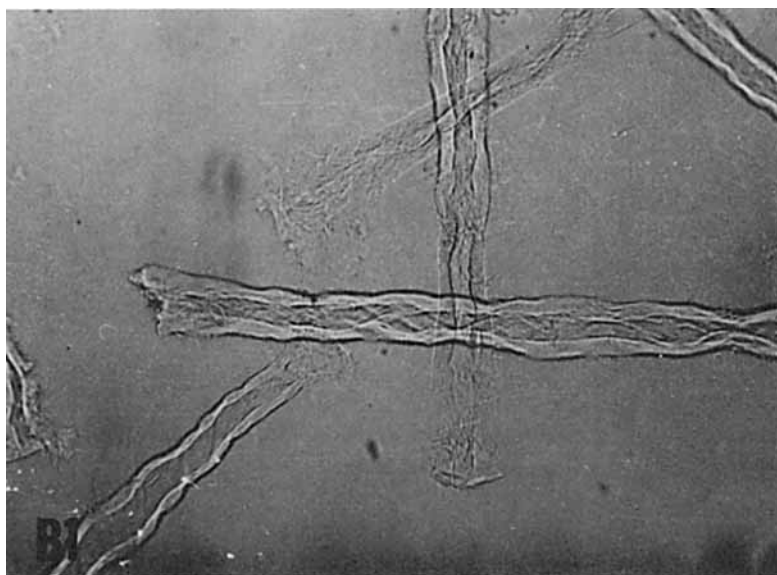Fig. 5.   (*Continued from the previous page.*)
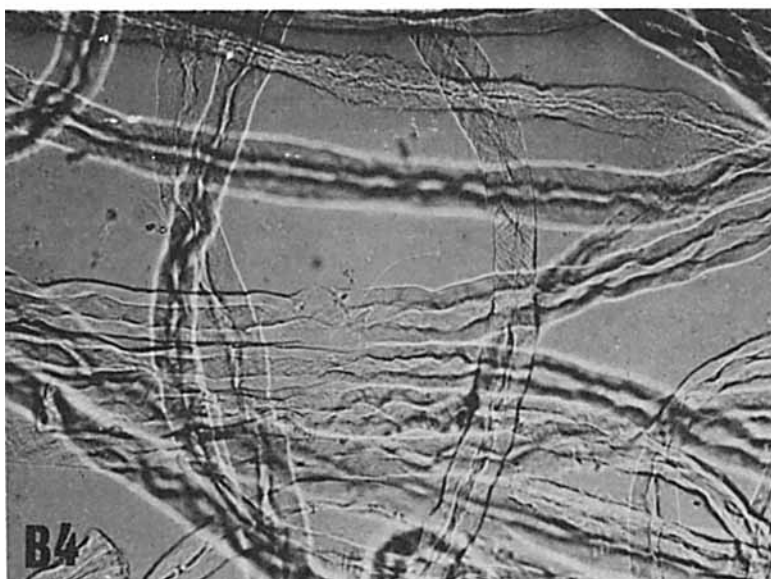
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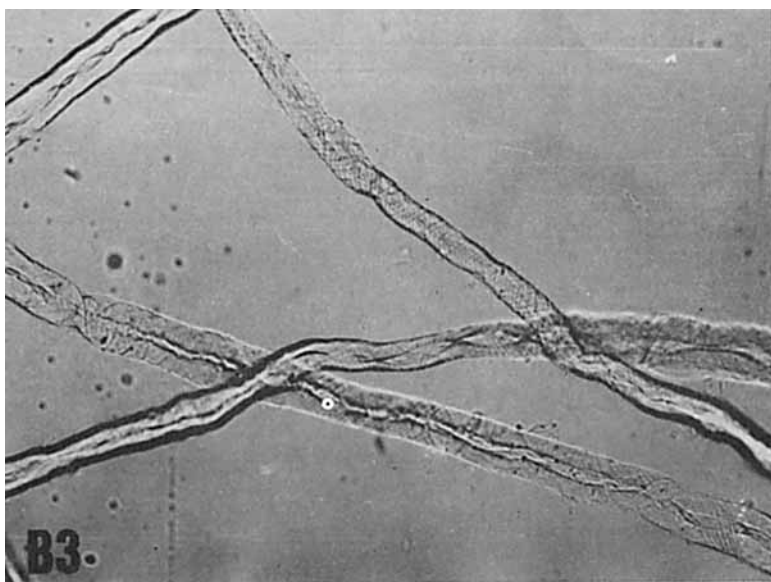
Fig. 5. (*Continued from the previous page.*)

TABLE II
Typical Analyses of Diquaternary Ammonium Cellulose Salts

| | Nitrogen Content | | Halide analyses as % conversion | | |
	(%)	(meq/g)	Wet analysis	Specific ion	Potentiometric titration
1. DEAE–cellulose	1.69	1.21	—	—	—
2. DEAE (1) + BrC$_5$H$_{10}$Br	1.70	1.21	75	90	90
3. DEAE–cellulose	2.58	1.84	—	—	—
4. DEAE (3) + BrC$_5$H$_{10}$Br	2.50	1.80	70	92	92
5. DEAE–cellulose	3.50	2.50	—	—	—
6. DEAE (5) + BrC$_5$H$_{10}$Br	3.41	2.47	90	100	100
7. DEAE (3) + IC$_5$H$_{10}$I	2.57	1.83	100	100	—
8. No. 7 + NaSCN	4.64	3.17	100 (4.57% S)	100	100
9. DEAE (3) + CH$_3$I	2.37	1.68	100	100	100
10. No. 9 + NaSCN	4.86	5.47	100 (5.70% S)	100	—

quaternaries of high N content are insoluble in cuene even when the anion is the thiocyanate. The micrographs in Figure 7 are illustrative of fibers from a diquaternary ammonium thiocyanate of 4.47% N after immersion in oil, water, and cuene. A DEAE–cotton of 2.67% N dissolves in 0.5M cuene, but, when only 23% converted to a diquaternary diborohydride, it is insoluble in cuene as shown in the micrograph in Figure 8.

Penetration and reaction of the reagent chemicals within the fiber was shown by scanning electron microscopy and energy dispersive X-ray analyses of fiber cross sections from DEAE fibers that had been exchanged with CuCl$_2$ and of fiber cross sections from a quaternary thiocyanate fabric. In Figure 9 the fiber cross section (a) of the CuCl$_2$-exchanged DEAE fiber and the Cu Kα (b) and Cl Kα (c) dot maps show the copper chloride to be distributed throughout the fiber. The cross section from the thiocyanate fiber (a) shown in Figure 10 and its sulfur Kα dot map (b) indicate that the thiocyanate exchange occurred throughout the fiber since sulfur is continuously distributed from primary wall to lumen.

Data in Table III show that, in nonaqueous media, the I$^-$ ion was most easily displaced by $\overline{BH}_4$ ions. The Cl$^-$ ion was hardest to displace from the monoquaternary salts. It was harder to displace the Cl$^-$ from the diquaternary chlorides than from the monoquaternary chloride. In every case, even with partial conversion, the borohydride salts were more dispersible in water than the corresponding halide forms.

For both monoquaternary and diquaternary ammonium celluloses, the relative amounts of quaternary ammonium groups and tertiary ammonium groups were calculated from the relative intensities of the peaks at 402 and
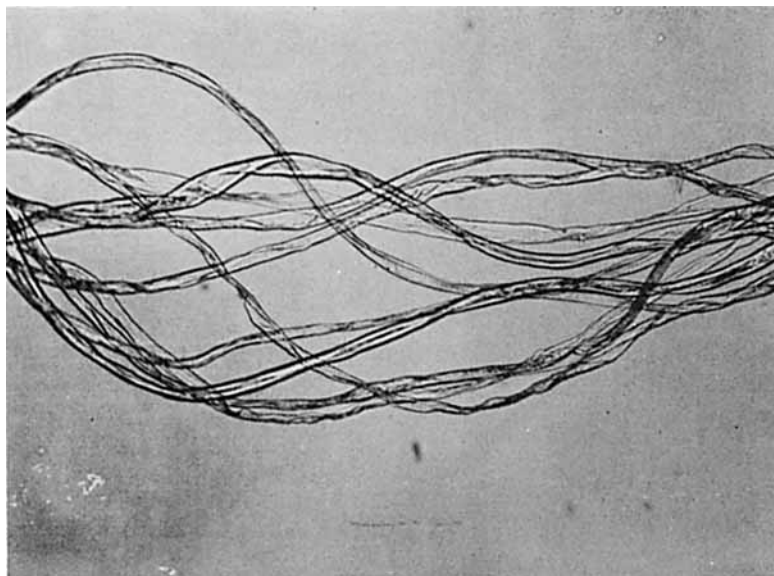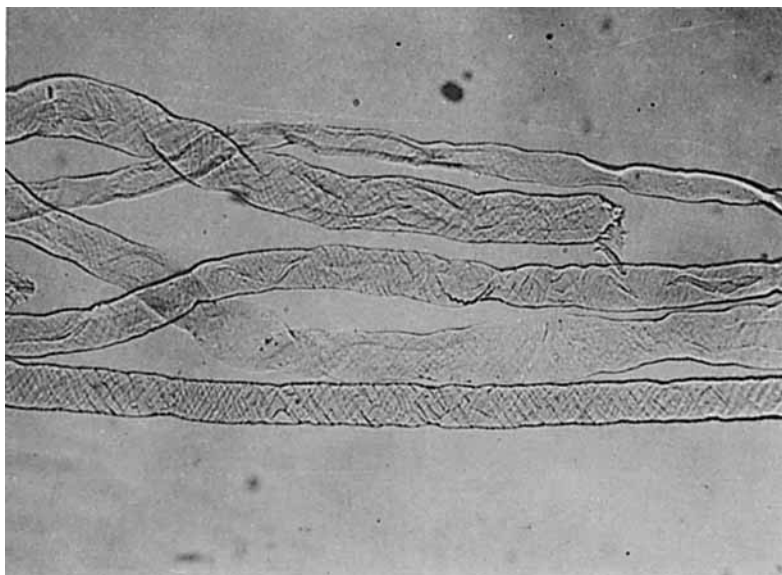
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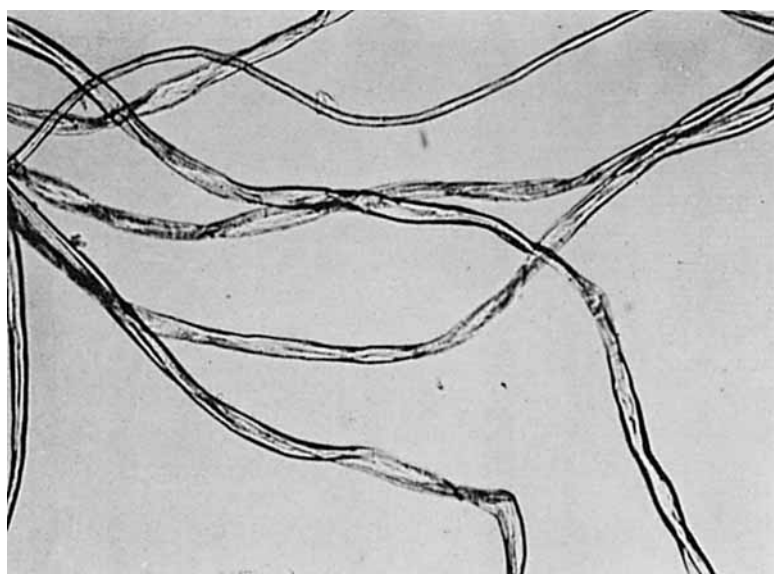
(b)

Fig. 6. Optical micrographs of fibers after immersion in mineral oil (a), water (b), and $0.5M$ cuene (c). Fibers from a DEAE–cotton of 0.67% N after reaction with diiodopentane to form a diquaternaryammonium cellulose iodide.
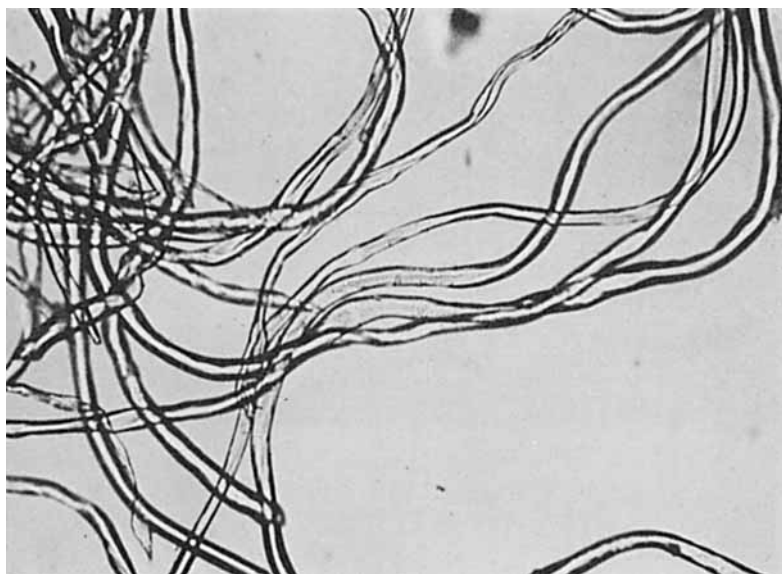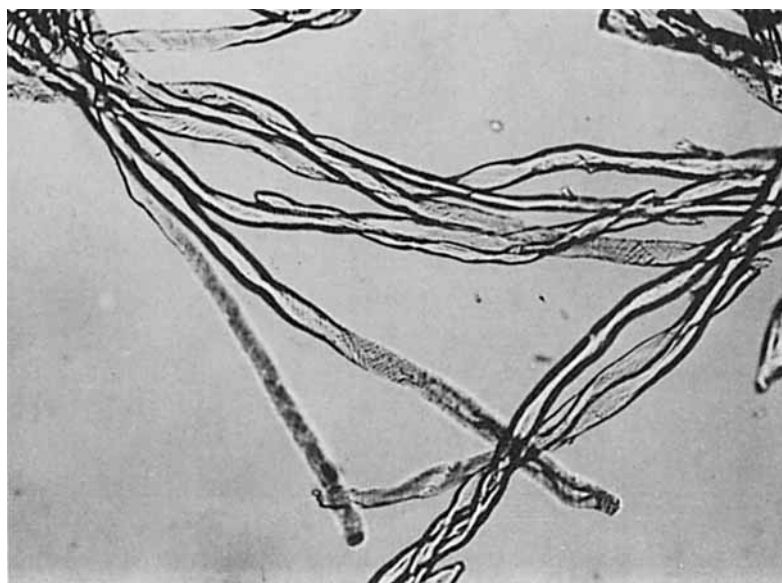
(c)

Fig. 6.   (*Continued from the previous page.*)

(a)

Fig. 7.   Optical micrographs of fibers after immersion in mineral oil (a), water (b), and 0.5M cuene (c). Fibers from a DEAE–cotton of 4.47% N that was reacted with diiodopentane to form the diquaternaryammonium cellulose iodide and then converted to the thiocyanate form in nonaqueous media.
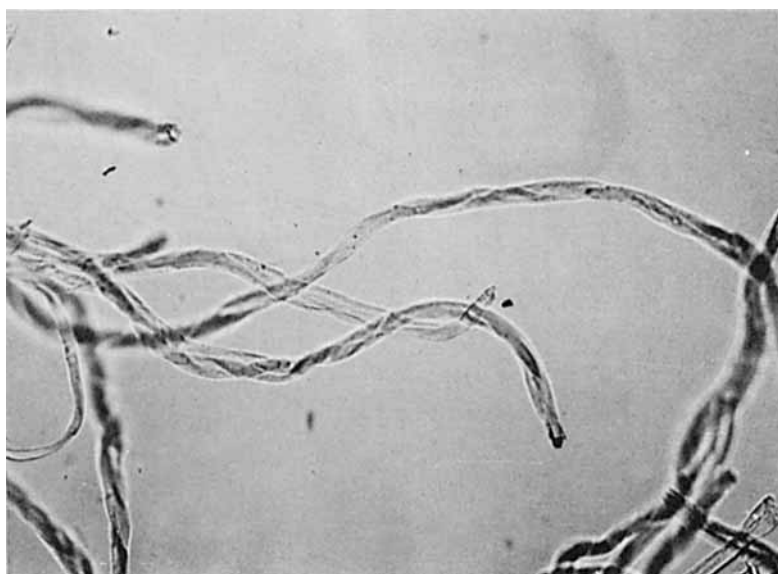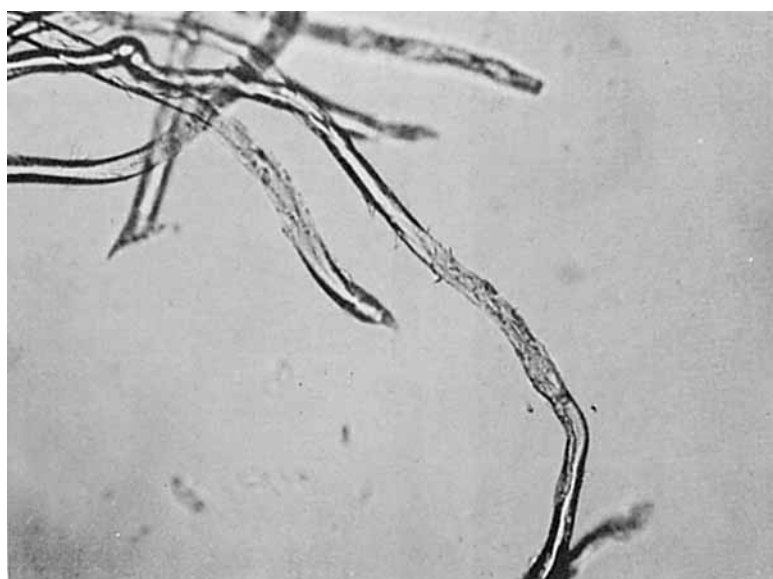
(b)

(c)

Fig. 7. (*Continued from the previous page.*)

(a)

(b)

Fig. 8.   Optical micrographs of fibers after immersion in mineral oil (a), water (b), and 0.5M cuene (c). Fibers from a DEAE–cotton of 2.6% N that was only 23% converted to the diquaternaryammonium diborohydride in nonaqueous media.

(c)

Fig. 8. (*Continued from the previous page.*)
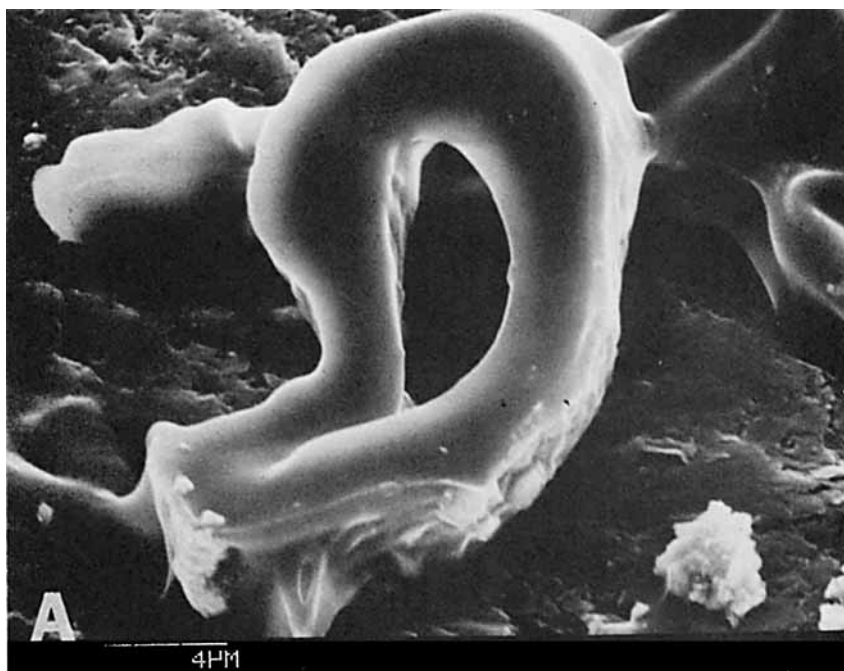
Fig. 9. Scanning electron micrograph of a cross section (A) of a $CuCl_2$ exchanged DEAE cotton fiber and its EDX Cu $K\alpha$ (B) and Cl $K\alpha$ (C) dot maps.
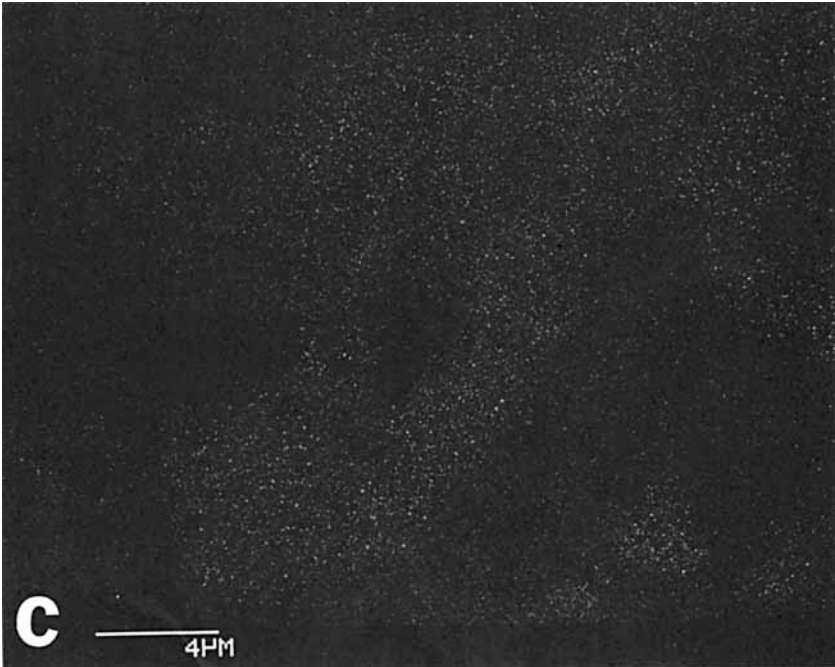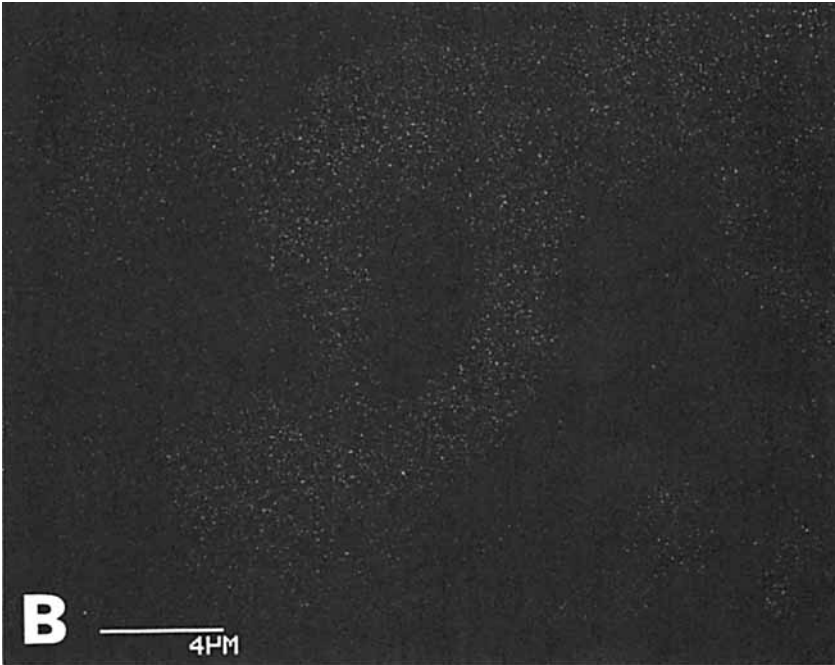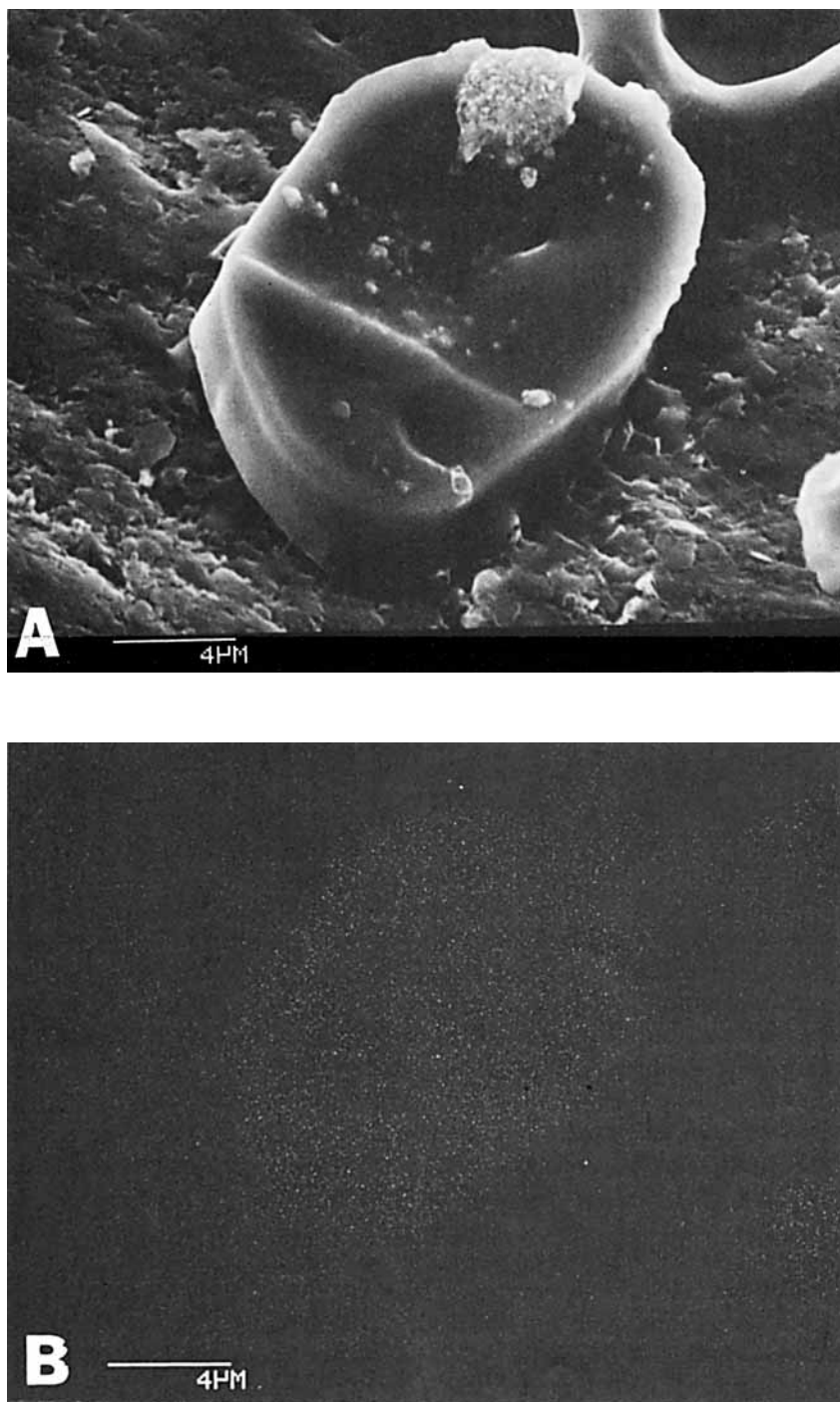
Fig. 9.   (*Continued from the previous page.*)

Fig. 10. Scanning electron micrograph of a cross section (A) from a thiocyanate exchanged quaternary cellulose cotton fiber and its S Kα (B) dot map.

TABLE III
Displacement of Halide by BH_4 in Nonaqueous Media

Exchanger	N^a (%)	B^a (%)	Conversion (%)
$\begin{array}{c} C_2H_5 \\ \mid \\ CellOC_2H_4\overset{+}{N}CH_3I^- \\ \mid \\ C_2H_5 \end{array}$	2.62	2.13	100
$\begin{array}{c} C_2H_5 \\ \mid \\ CellOC_2H_4\overset{+}{N}CH_3Cl^- \\ \mid \\ C_2H_5 \end{array}$	2.64	1.17	60
$\begin{array}{c} C_2H_5 \\ \mid \\ CellOC_2H_4\overset{+}{N}CH_3Br^- \\ \mid \\ C_2H_5 \end{array}$	2.20	1.53	90
$\begin{array}{cc} C_2H_5 & C_2H_5 \\ \mid & \mid \\ CellOC_2H_4\overset{+}{N}(CH_2)_5\overset{+}{N}C_2H_4OCell2Cl^- \\ \mid & \mid \\ C_2H_5 & C_2H_5 \end{array}$	2.92	0.60	26
$\begin{array}{cc} C_2H_5 & C_2H_5 \\ \mid & \mid \\ CellOC_2H_4\overset{+}{N}(CH_2)_{10}\overset{+}{N}C_2H_4OCell2Cl^- \\ \mid & \mid \\ C_2H_5 & C_2H_5 \end{array}$	3.24	1.10	47

^{a} Wet analysis for N and B.

399 eV respectively, in the ESCA spectra. These ratios agreed with the ratio of quaternary to tertiary amino groups as determined from potentiometric titration curves of the exchangers. Typical data obtained by the two methods are given in Table IV.

Degree of conversion to a given salt form was also checked with specific ion electrodes. For example, a DEAE cellulose of 2.58% N (1.85 meq/g) when reacted with dibromopentane gave a quaternary bromide that was subsequently subjected to specific ion analysis for the Br^- ion in a solution of excess Cl^- ions. A sample weighing 0.5917 g (1.09 meq/g) of N in 100 mL gave a reading of 1.09×10^{-2} meq/mL. The theoretical molarity of Br^- ion was calculated to be $1.20 \times 10^{-2}M$. Similar analyses of a 0.3833 g sample of a DEAE–cellulose quaternized with C_2H_5Br yielded a $7.65 \times 10^{-3}M$ Br^- solution (theory for 100% conversion was $9.38 \times 10^{-3}M$).

Our selection of quaternary ammonium substituents as a means of changing the entropy or order of the cellulose–water matrix was based on the following well-known facts: (1) alkyl groups of quaternary ammonium salts form hydrophobic bonds mainly because of entropy changes associated with water-structuring around nonpolar groups,[14] and (2) structuring of water occurs in the accommodation of quaternary ammonium ions and large nonhydrated anions in cagelike structures.[15] The water of hydration in quaternary ammonium bromides (QBr · $32H_2O$) is highly structured,[16] and Frank and Evans[17] showed

TABLE IV
Relative Amounts of Quaternary and Tertiary Amines

	N_{1s} Binding energy (eV)		Ratio[a]	$\dfrac{NR_4^+}{:NR_3}$
	N^+R_4	$R_3N:$	ESCA	Titrations
1. DEAE cellulose	401	399	0.9	0.9
2. DEAE (1) $+CH_3I$	401	399	3.4	3.0
3. DEAE (1) $+C_2H_5Br$	402	399	3.0	3.0
4. DEAE (1) $+Br_2C_2H_4Br$	402	399	1.6	1.5
5. DEAE cellulose	401	399	0.3	0.3
6. DEAE (5) $+CH_3I$	402	399 (tr)	9.0	9.0
7. Sample 6 $+Cl^-$	402	399 (tr)	9.0	8.8

[a] $NR_4^+/:NR_3$ is the ratio of intensities of peaks in ESCA spectra for E_{BE} of 402 and 399 eV; for potentiometric and/or conductometric titrations, ratio is meq/g titrant required to titrate strong base quaternary to meq/g required to titrate weak base DEAE component.

that large anions associated with quaternary groups caused water to become more structured around these salts. The importance of the anion associated with the quaternary group has been exemplified via the conductance and activity coefficients of quaternary halides.[18] Lindeman and Boyd[19] reported an increase in activity coefficients of the chlorides but a decrease in activity coefficient of the bromides and iodides as the size of the quaternary ammonium group increased. Wen and Saito[20] concluded that the stoichiometric composition of tetrabutyl quaternary bromide in solution was $(C_4H_9)_4NBr \cdot (35 \pm 2)H_2O$, and that the water was highly structured.

Magne and co-workers[21,22] in a calorimetric study showed that water hydrogen-bonded to hydroxyl groups of cellulose is more tightly bound than is water in capillaries of cotton and, in fact, has a more ordered structure than does bulk water.

Usually, explanations of the solubility of cellulose or its dispersion in various salt solutions is based on hydration of ions. Collins and Williams[23] first suggested that hydrated ions affected the amount of swelling of cellulose by water-containing salts. Heuser and Bartunek[24] reported that the maximum degrees of swelling of cellulose in alkali solutions are in the same order as the degrees of hydration of the metal ions. Cellulose was reported to be more soluble in solutions of salts having a small and highly hydrated cation such as Li^+ and a rather large anion such as $\overline{SCN}$.[25] In these early works it was theorized that the hydrated ions carried water into the cellulose matrix as they coordinated with cellulosic hydroxyl groups. Usually, high concentrations of such salts were required to dissolve or disperse cellulose.

Chedin and Marsaudon[26] emphasized the importance of entropy changes in the calculation of free energy of swelling of cotton. Phillips and colleagues[27] considered the H-bonded system of anhydroglucose units within the cellulose matrix and the interactions of cellulosic hydroxyls with donor and acceptor

centers of solvents capable of H-bonding via inter- and intramolecular H bonds. These investigators considered solubility parameters of the solvent as discussed by Hansen.[28] According to the theory, swelling or dissolution occurs when the solubility parameters of the solute and solvent are similar. Or in the case of quaternary ammonium celluloses, when the surface energy properties of the cellulose modification are similar to the bulk energy properties of the solvent, it will dissolve or swell. Qualitative observations on the solubilities and dispersions of quaternary ammonium celluloses in water are consistent with the theories of "water structure enforced ion pairing." The anion associated with a given quaternary ammonium cation is an important factor in determining the degree of water structuring within the cellulose matrix and the solubility parameters of the product.

CONCLUSIONS

Modification of cotton cellulose by introduction of quaternary ammonium cations changes the surface properties of cotton and its attraction for both hydrophobic and hydrophilic substances. Cotton and other celluloses have historically been dissolved or swollen by treatment with aqueous solutions of salts associated with the lyotropic series. Usually, rather large concentrations of ions are required when the salts are in the solvent. Direct substitution of quaternary ammonium groups and their subsequent association with large polarizable anions even at dilute concentrations promote the swelling and/or dissolution or dispersion of cellulose. Association of the quaternary ammonium groups with the hydrated chloride anion results in modified cottons that are insoluble in water but which scavenge both hydrophobic and hydrophilic moieties. Alteration of the surface properties of cellulose with quaternary ammonium groups and their associated anions is potentially useful for subsequent chemical modifications of cellulosic products.

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